

Kinetics of Pyromorphite Formation as Influenced by Aging

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Beamline(s): X11A

Introduction: Changes in the crystal chemistry of solids as a result of increased residence time in the natural environment may explain the low bioavailability of metals in soils and sediments [1]. In this study we examined the formation of a stable Pb phosphate, pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) via X-ray absorption fine structure (XAFS) spectroscopy and complimented the results with high-resolution thermogravimetric analysis (HRTGA). Immobilization of Pb in contaminated soils via phosphorus amendments may prove to be cost-effective and environmentally safe. Although XAFS showed little differences in the crystal structure during the aging process, HRTGA demonstrated that the thermo-stability did vary.

Methods and Materials: Pyromorphite was created by mixing 0.25 M PbCl_2 and 0.15 M H_3PO_4 in 2 L HDPE bottles at a pH of 7.0 and under a N_2 atmosphere. The bottles were allowed to age for prescribed times and the pH was maintain throughout the experiment. Aging times ranged from 1 hour to 1 year. At the end of the set aging interval, the solid was collected by centrifugation and freeze-dried to stop the aging process. The solid samples were then analyzed by XAFS and HRTGA.

Results: Figure 1 shows the RSFs for the aged pyromorphites and fits to these data suggest Pb is octahedrally coordinated in the first shell with 6 oxygen atoms (3 @ 2.62Å and 3 @ 2.83Å). The second shell data comprised of three additional oxygen atoms located at approximately 3.0Å as well as three phosphorus atoms at 3.4Å. These data are in line with natural pyromorphite. While XAFS showed little difference in the chemical environment of pyromorphite, HRTGA did indicate some differences primarily at the early aging periods of 1-hour and 1-day. Figure 2 shows the derivatives of weight loss versus temperature for the aged pyromorphites. Typically, as stability increases, weight loss decreases and this is noted in Figure 2 by decreasing peak intensities for the aged pyromorphite at approximately 590 °C.

Conclusions: The data collected in this study show that pyromorphite formation is kinetically rapid and crystallizes to a stable mineral in a short time period. These are ideal conditions for an in-situ, immobilization remediation technique [2-4]. XAFS identified the mineral phase as pyromorphite based on coordination environment and interatomic bond distances. HRTGA investigations suggested that at aging times of 1-hour and 1-day, the pyromorphite crystals have not undergone complete Ostwald ripening, however, little difference was observed between the 1-week and 1-year aged samples indicating that the aging process occurs within one week.

Acknowledgments: The research results presented herein do not, necessarily, reflect Agency policy. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

References:

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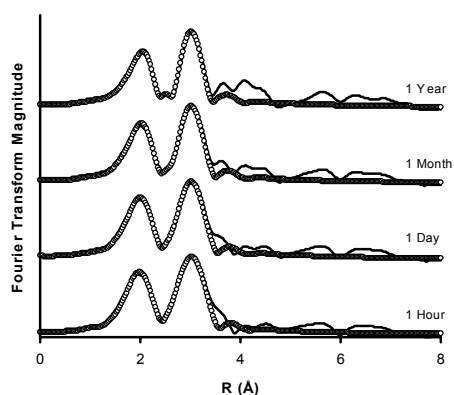


Figure 1. RSFs of aged pyromorphite.

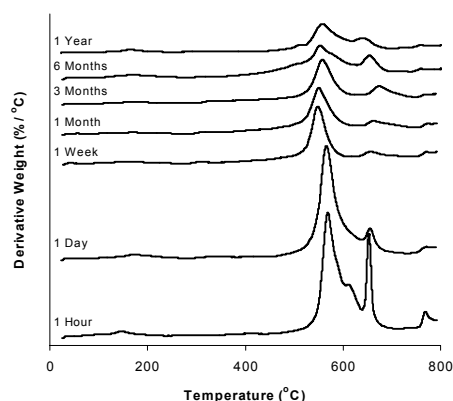


Figure 2. HRTGA of aged pyromorphite.